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ADVANCED WASTE TREATMENT SEMINAR, SESSION I, NITROGEN REMOVAL FROM WASTEWATER, HELD AT SAN FRANCISCO, ON OCTOBER 28-29, 1970

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CLEAN WATER

SESSION I

NITROGEN REMOVAL

ADVANCED WASTE TREATMENT SEMINAR

San Francisco
October 28 & 29
1970

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Ammonia & nitrate are the principle forms of nitrogen in waste water. Ammonia is converted to nitrate by biological oxidation. Denitrification reduces it levels & high BOD in surface waters. Nitrates are reduced to nitrogen gas by bacteria when organic matter limits the oxygen supply. Both compounds are algal nutrients but ammonia is much more toxic than nitrates. The best developed method for control of nitrogen compounds is biological oxidation to nitrate followed by denitrification with the aid of methanol.

Ammonia stripping at high pH in packed towers following lime treatment is effective but cannot be used during freezing weather as the may suffer from serious scale problems. Selective ion exchange of ammonia with limited regeneration may be practical but the process is still in the pilot stage. Several other processes are being studied. A bibliography of pertinent references is attached.

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ADVANCED WASTE TREATMENT SEMINAR

KABUKI THEATRE
1881 POST STREET
SAN FRANCISCO

OCTOBER 28-29, 1970

JOINTLY SPONSORED BY
CALIFORNIA STATE WATER RESOURCES CONTROL BOARD
AND
PACIFIC SOUTHWEST REGIONAL OFFICE
FEDERAL WATER QUALITY ADMINISTRATION

PROGRAM

OCTOBER 28 - MORNING

9:00 AM Introduction - Jerome P. Gilbert

SESSION I NITROGEN REMOVAL

Moderator: Professor Perry L. McCarty

9:30 AM Measurement and Forms of Nitrogen and Phosphorus
Edwin F. Barth

10:00 AM Ammonia Stripping - Robert B. Dean

10:45 AM Biological Nitrification - Denitrification
Edwin F. Barth

11:15 AM Ammonium Specific Ion Exchange - Robert B. Dean

11:45 AM Summary - Professor McCarty

CONTENT

MEASUREMENT AND FORMS OF NITROGEN AND PHOSPHORUS
Edwin F. Barth

NITROGEN REMOVAL FROM WASTEWATER
Advanced Waste Treatment Research Laboratory
Cincinnati, Ohio

The Seminar also included the below sessions:

Session II Phosphorus Removal
Session III Removal of Solids and Organics
Session IV Combined Treatment and Application

MEASUREMENT AND FORMS OF NITROGEN AND PHOSPHORUS

EDWIN F. BARTH 1/

-/-

This topic is placed first on the agenda because without a basic understanding of the chemistry of nitrogen and phosphorus and good analytical control of our nutrient removal processes, we will gain little from our efforts.

My remarks today will be directed to nitrogen and phosphorus chemistry from a treatment standpoint.

Phosphorus and nitrogen have many similarities and some important dissimilarities.

The periodic table of the elements, given in Figure 1, shows that nitrogen and phosphorus are in the same chemical family and would be expected to have similar chemical reactions. Both do have three and five as major chemical valences, both are non-metals, both form similar types of compounds. Also showing the family relationship is arsenic, the third member of the family, which is a serious interference in the phosphomolybdic assay of phosphorus, leading to high results if not accounted for. While not a serious interference in flowing water, it can be significant in sediment analysis of lakes that have had arsenate spray for algae control, or have received run-off from fields using arsenate spray for insect control. Industrial waste from transistor manufacture can also be a source of interferring elements.

A major difference between nitrogen and phosphorus is that elemental nitrogen is a stable gas, while phosphorus is a reactive solid. Even though their chemical reactions are similar, the resulting compounds vary significantly. Most nitrogen compounds of interest from a treatment standpoint are water soluble, while most phosphorus compounds are insoluble.

The elements carbon, sulfur, oxygen, and nitrogen that are near phosphorus in the table are vital to life processes and form gaseous compounds in biological systems. Figure 2 considers these elements from a treatment standpoint. Oxygen, sulfur, hydrogen, carbon, and nitrogen at some point in a treatment sequence, either in an aerobic or anaerobic environment, can go through oxidation and reduction reactions to a gaseous product which is lost to the atmosphere. Phosphorus compounds enter a treatment plant in their highest oxidized form and cycle between organic and inorganic forms. No common biological systems reduce phosphate. Phosphorus is conserved in the system. This is the reason the chemistry of phosphorus is important in eutrophication. Once in an environmental system, phosphorus will cycle endless unless it is completely separated from the system by physical isolation, insolubility, or wash-out by dilution. Phosphorus cannot be depended upon to vent to the atmosphere. In this context it must be emphasized that to fully evaluate the environmental influence of phosphorus, a determined effort must be made to measure all the phosphorus contributing to a situation. Because of this cyclic pattern, only a total phosphorus analytical procedure can indicate the reservoir of phosphorus available. While many phosphorus compounds are considered insoluble, microenvironments can have a profound influence. The dissolution of the insoluble hydroxapatite of teeth by localized activities of microorganisms is an example. Some of the most desirable fertilizers for plant growth are phosphorus compounds that are insoluble but release phosphorus at a low rate in response to the environmental demand. Certainly the entire substra of a receiving water does not have to be considered as an active part of the cycle, but cognizance of the importance of the organic-inorganic solids deposited as sludge banks, which foster anaerobiosis,

is necessary. In treatment efforts to remove phosphorus and control eutrophication in receiving waters, measures of soluble ortho-phosphate in filtered samples cannot be solely relied upon.

From the standpoint of measuring treatment efficiency, we must measure total phosphorus into the process and total phosphorus out of the process-whatever system it may be, either biological or strictly chemical precipitation. With wastewater samples, total phosphorus refers to a wet ashing procedure employing sulfuric and an oxidizing agent. For resistant samples such as primary sludge or biological sludge the use of perchloric acid may be necessary. A second procedural test that may be helpful is total soluble phorphorus. In this case the sample is filtered before wet ashing. This will by-pass the efficiency of the final liquid-solids separation unit process and provide information on advantages to be gained by improved liquid-solids separation. Two points must be kept in mind, first the total phosphorus assay should be used to judge actual operating efficiency, and second the total soluble assay is procedural so that the filter medium must be specified.

The phosphorus procedure given in Standard Methods is designed for boiler water analysis and will not register all forms of phosphorus present in wastewater samples.

By various procedural methods and analytical conditions as shown on Tables I and II, the phosphorus content of wastewater can be broken down into fourteen fractions. For instance #4 minus #1 from Table I, would represent fraction 11, particulate ortho-phosphate, on Table II.

In my estimation schemes like this are not necessary for treatment control and confuse rather than clarify. However, I do realize that in certain biological investigations or special surveys, specialized manipulations such as this could be helpful, but the interpretation of the data must be tempered with a knowledge of the limitations of the analytical procedures.

My reason for basing treatment efficiency solely on total phosphorus can be seen by reference to Tables III and IV. We can expect to find all these forms of phosphorus in wastewaters and sludges. With such a diversity of structures and solubilities we must ensure that we look at the total picture. This can only be done by employing a total phosphorus analysis, in this way all phosphorus compounds are converted to orthophosphate which is what reacts with the final reagent to quantify the procedure. The most common analytical procedure now used for phosphorus is the phosphomolybdic procedure. This test is an empirical operational procedure and all variables must be controlled. Time of reaction, temperature, reductant and acid concentration are important considerations. Table V shows, for example the effect of final acid concentration on color development. If acidity is not high enough auto-reduction of molybdate occurs, giving high blanks. If too acid the phosphomolybdic reduction is inhibited and silicate can interfere.

With the intense national and international interest in phosphorus removal, there is a real need for development of a referee method for phosphorus.

The state of the art for phosphorus analysis is at such a stage that the reagents and test conditions cannot sharply differentiate ortho, poly, organic, or mineral phosphorus. There is only one logical way to report results of phosphorus analyses and that is as elemental phosphorus, just as we have been doing with nitrogen for many years.

From the historical point of view of sanitary chemistry nitrogen analyses have seniority over suspended solids and B.O.D. Classical British and early American practice used the nitrogen series determinations to control biological processes and trace wastewater pollution.

The B.O.D. gained ascendancy over the nitrogen series for two reasons. First, the analysis was not as tedious - simply measure dissolved oxygen before and after an incubation period. Second, the biological processes were made to look more efficient in satisfying biochemical oxygen demand when using B.O.D. rather than complete nitrification as an endpoint. Acceptance of the 5-day B.O.D. has shifted the burden of satisfying nitrogenous oxygen demand from the treatment plant into the receiving water.

With the critical D.O. sag that is occurring in many waters that are receiving biologically treated effluents from efficient treatment plants - on the basis of 5-day B.O.D. - and the importance of nitrogen as a nutrient for algae growth, we again enter an era where the nitrogen series determinations are important.

As with phosphorus, nitrogen occurs in wastewaters in many forms, such as ammonia, organic nitrogen, nitrite nitrogen, and nitrate nitrogen. There is one big difference, the analytical procedures for nitrogen are specific

for each form. Even though the different forms are measured specifically, the results are given as elemental nitrogen to make it easier to account for nitrogen in a given system.

When quantifing nitrogen the whole series must be determined to get reliable data. Figure 3 is an idealized curve of biological nitrogen transformations in a batch system under aeration with a small initial inoculum. It can be seen that no single nitrogen assay can give complete quantitation at any instant. This fact has been overlooked many times and a great amount of otherwise excellent work on stream surveys, lake studies, and plant monitoring is absolutely valueless from a nitrogen standpoint. The importance of determining all forms of nitrogen is also illustrated in Table VI. A high-rate activated sludge effluent was mixed with a well nitrified effluent to force denitrification to occur. The oxidized nitrogen values show efficient denitrification, but summation of the total nitrogen series shows a much lower over-all efficiency. The literature is replete with investigators who became so interested in one facet of their study that they neglected the overall importance of strict analytical control.

Perhaps the other most common error in nitrogen analysis is the preservation of samples. Standard Methods is in gross error in recommending adding sulfuric acid for preservation of nitrite samples. Figure 4 shows the classical Van Slyke reaction. Nitrite in the presence of acid reacts with primary amines, or ammonia, to form free nitrogen gas which is lost from the system. Nitrite cannot be preserved with acid. Freezing is the best method for preserving the nitrogen forms.

As one last point on matching analytical control to desired results the Drinking Water Standards for nitrate nitrogen is interesting. The recommended limit of nitrate nitrogen is 10 mg/l. However, the actual toxicant is nitrite which causes methemoglobinemia. Since the nitrite and nitrate analytical procedures are specific for each form; if only nitrate is determined as indicated by the Standard a toxic level of nitrite could go undetected. As we increase the use of ground water recharge the chance of oxidized nitrogen build-up increases, and as has been shown in Figure 3, we can never be sure at what stage the nitrogen transformations are in unless we use the proper analytical procedures. The recommended limit should be based on nitrite plus nitrate.

Pertinent to the topic of measurement and forms of nitrogen and phosphorus is the subject of automated analytical procedures. Automated instruments are marvels of electronic precision but they are analytical idiots. With the increasing pressure to collect more frequent data on a larger number of parameters automated procedures are needed. The operator who cares for and operates these instruments must understand their intellectual level. Any one who has taken an automated analytical procedure from the research stage through final evaluation, and on site testing soon realizes he had to become a better informed chemist in order to instruct the machine.

1/ Edwin F. Barth, Chemist, Biological Treatment Research Program, Advanced Waste Treatment Research Laboratory, Cincinnati, Ohio

Element	Symbol	Valences	Usual form
Nitrogen	N	3, 5, 1, 2, 4	Gas
Phosphorus	P	3, 5, 1, 4	Waxy solid
Arsenic	As	3, 5	Metallic solid

Compounds with similar properties

↑ Acid strength	↑ Reactivity	↑ Unstable nature	↑ Stable nature
HNO_3	N_2O_3	NCl_3	NH_3
H_3PO_4	P_2O_3	PCl_3	PH_3
H_3AsO_4	As_2O_3	$AsCl_3$	AsH_3

Similar compounds with different properties

Soluble: $Ca(NO_3)_2$ $Al(NO_3)_3$ $Fe(NO_3)_3$

Insoluble: $Ca_3(PO_4)_2$ $AlPO_4$ $FePO_4$ $(NH_4)MgPO_4$

FIGURE I

7a

ELEMENTS AND BIOLOGICAL TREATMENT

ELEMENT	BIOLOGICAL REACTION	RESULT OF TREATMENT NET LOSS
OXYGEN	OXIDATION AND/OR REDUCTION	CO_2 CH_4
CARBON		
HYDROGEN		H_2 H_2O
NITROGEN		N_2
SULFUR		H_2S
PHOSPHORUS	NO OXIDATION NO REDUCTION	NO LOSS: ORGANIC PHOSPHORUS ⇅ INORGANIC PHOSPHORUS

FIGURE 2

TABLE I

Determination of Various Phosphorus Forms

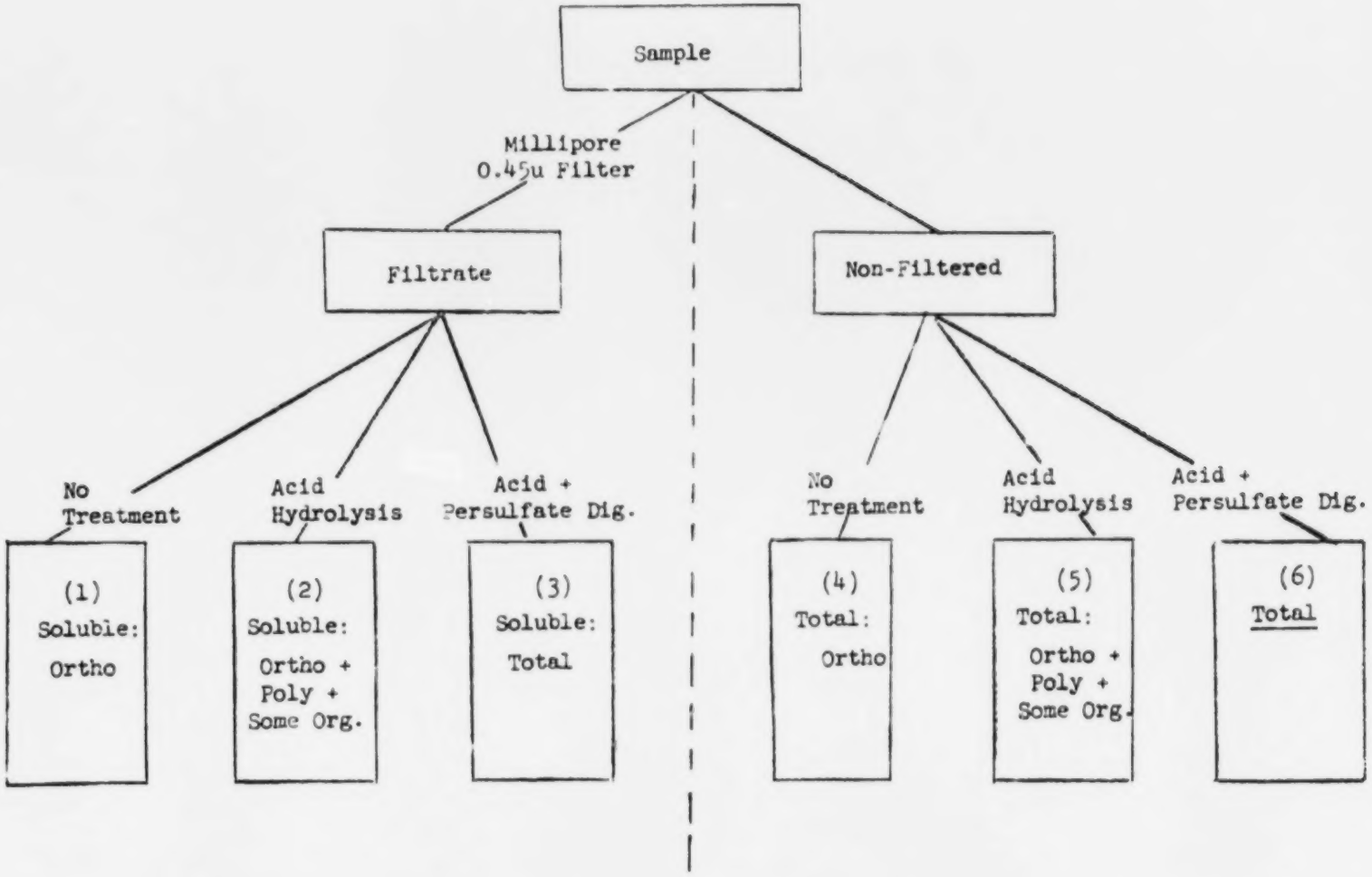

TABLE II

Data Treatment	Phosphorus Components Determined
	A. Soluble Forms
1	1) ortho
2	2) ortho + poly + some org's.
3	3) total
2 - 1	4) poly + some org's.
3 - 2	5) most org's.
	B. Total Forms
4	6) ortho
5	7) ortho + poly + some org's.
6	8) total
5 - 4	9) poly + some org's.
6 - 5	10) most org's.
	C. Particulate Forms
4 - 1	11) ortho
(5-4) - (2-1)	12) poly + some org's.
(6-5) - (3-2)	13) most org's.
6 - 3	14) total

TABLE III

Forms and Measurements of Phosphorus

Phosphoric Anhydride	P_4O_{10} (usually calculated as P_2O_5)

Orthophosphates Found in Water

Phosphoric acid	H_3PO_4 below pH 2.2
Dihydrogen phosphate ion (monovalent)	$H_2PO_4^-$ from pH 2.2 to 7.2
Monohydrogen phosphate ion (divalent)	$HPO_4^=$ from pH 7.2 to 12.4
Phosphate ion (trivalent)	$PO_4^{\equiv}$ above pH 12.4
Dicalcium phosphate	$CaHPO_4$ from pH 6 to 8

(Tricalcium phosphate, $Ca_3(PO_4)_2$, does not form in water)

Hydroxyapatite	$Ca_5OH(PO_4)_3$ above pH 7-8
Fluorapatite	$Ca_5F(PO_4)_3$ above pH 7

Aluminum hydroxide adsorbs $HPO_4^=$ from pH 5 to 10

Aluminate ion $Al(OH)_4^-$ forms above pH 10

Ferric hydroxide adsorbs $HPO_4^=$ above pH 4

Magnesium hydroxide flocculates colloidal phosphates above pH 10-11

Polyphosphates

All polyphosphates hydrolyze slowly to orthophosphates

Sodium Trimetaphosphate	$Na_3(PO_3)_3$ -- a ring compound
Sodium Polymetaphosphate	$(NaPO_3)_n$ -- a long chain

(there is no justification for the name "hexametaphosphate")

Sodium Pyrophosphate	$Na_4P_2O_7$
Sodium Tri Polyphosphate	$Na_5P_3O_{10}$

Organic Phosphates

Esters and anhydrides	$ROPO_3^=$, $ROPO_3PO_3^=$
Phosphagens	$RNPO_3^=$

Reference

(1) Van Wazer, J. R. Phosphorus and Its Compounds. Interscience 1958.

TABLE IV

PHOSPHORUS COMPOUNDS CLASSIFIED BY CHEMICAL AND SOLUBILITY RELATIONS(1)

Form	Water Soluble(2)	Insoluble(2)
1. Ortho phosphates $(PO_4)^{-3}$	Combined with monovalent cations such as H, Na, K, NH_4	Combined with multi valent cations such as CA^{+2} Al^{+3} Fe^{+3}
2. Poly phosphates $(P_2O_7)^{-4}$, $(P_3O_{10})^{-5}$ $(P_3O_9)^{-3}$ and others depending upon the degree of dehydration.	(a) as in 1 (above), but solubility decreases as molecular weight increases	(a) as in 1 (above) (b) multi P polyphosphates (high mol. wt.) including the "glassy" phosphates
3. Organic phosphorus R-P, R-P-R (3) (unusually varied nature)	(a) certain chemicals (b) degradation products (c) enzyme P (d) phosphorylated nutrients	(a) certain chemicals (b) cell mass, may be colloidal or agglomerated (c) soluble P sorbed by insoluble residues
4. Mineral phosphorus	(a) as in 1 (above), but solubility decreases for complex forms	(a) as in 1 (above) (b) geological P such as phosphosilicates (c) certain mineral complexes

(1) Table drawn from a lecture, "Determination of Phosphorus in the Aqueous Environment," by F. Ludzack, FWPCA Training Activities, Ohio Basin Region.

(2) Used to indicate usual state under common conditions.

(3) R represents an organic radical, P represents P, PO_4, or its derivatives.

TABLE V

Effect of Varing Sulfuric Acid - Ammonium Molybdate Ratio on Heteropoly Blue Color Development (Stannous chloride in glycerine reductant)

Acid Molybdate Reagent Composition		Normality* of acid in final 100 ml assay volume	Absorbancy (O.D.)	
Ammonium Molybdate gm/100 ml	Concentrated Sulfuric Acid ml/100 ml		Distilled Water	0.05 mg P Standard
2.0	5	0.072	> 2.0	> 2.0
2.0	10	0.144	0.805	1.00
2.0	15	0.216	0.260	0.580
2.0	20	0.288	0.036	0.475
2.0	25	0.360	0.004	0.415
2.0	30	0.432	0.000	0.365
2.0	35	0.504	0.000	0.345
2.0	40	0.576	0.000	0.252
2.0	50	0.720	0.000	0.060
2.0	60	0.864	0.000	0.012

*Calculated normality of H_2SO_4 in the 100 ml final volume produced by using 4.0 ml of the particular acid molybdate solution.

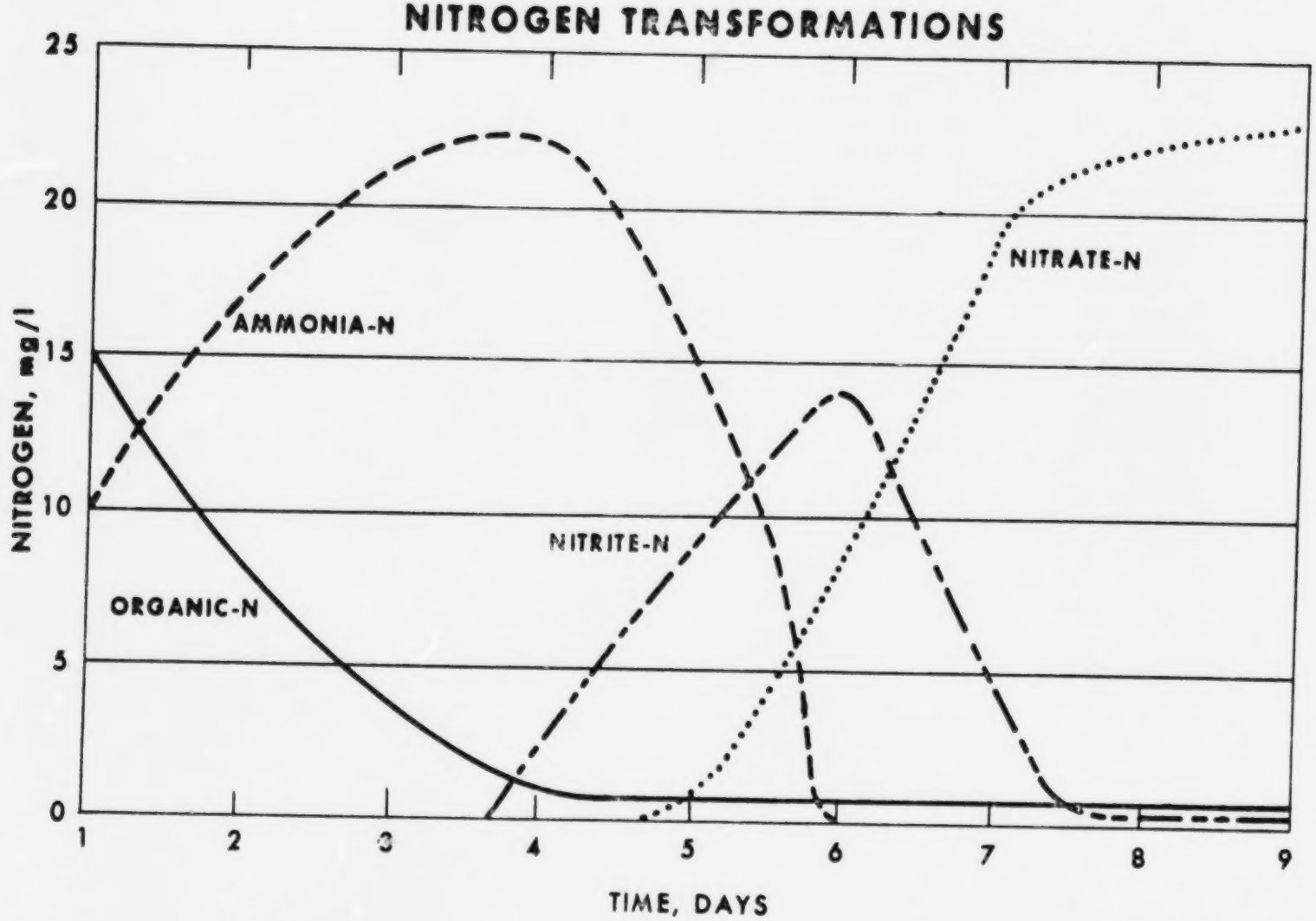
NITROGEN TRANSFORMATIONS
25
20
15
10
5
0
NITROGEN, mg/l
AMMONIA-N
NITRATE-N
NITRITE-N
ORGANIC-N
1
2
3
4
5
6
7
8
9
TIME, DAYS

FIGURE 3

TABLE VI

Nitrogen Forms in 1:1 Mixture of
High-Rate and Nitrified Effluents

Nitrogen Form	High-Rate Effluent	Nitrified Effluent	Denitrified Effluent	Oxidized Nitrogen Removal	Over-All Removal
Organic-N	5	2	3		
Ammonia-N	10	0	5		
NO_2-N	-	1 > 13	0.5 > 1.0		
NO_3-N	-	12	0.5	92%	
Sum	15	15	9		40%

VAN SLYKE REACTION

$$RNH_2 + NO_2^- \xrightarrow{\text{acid}} ROH + N_2\uparrow + H_2O$$

FIGURE 4

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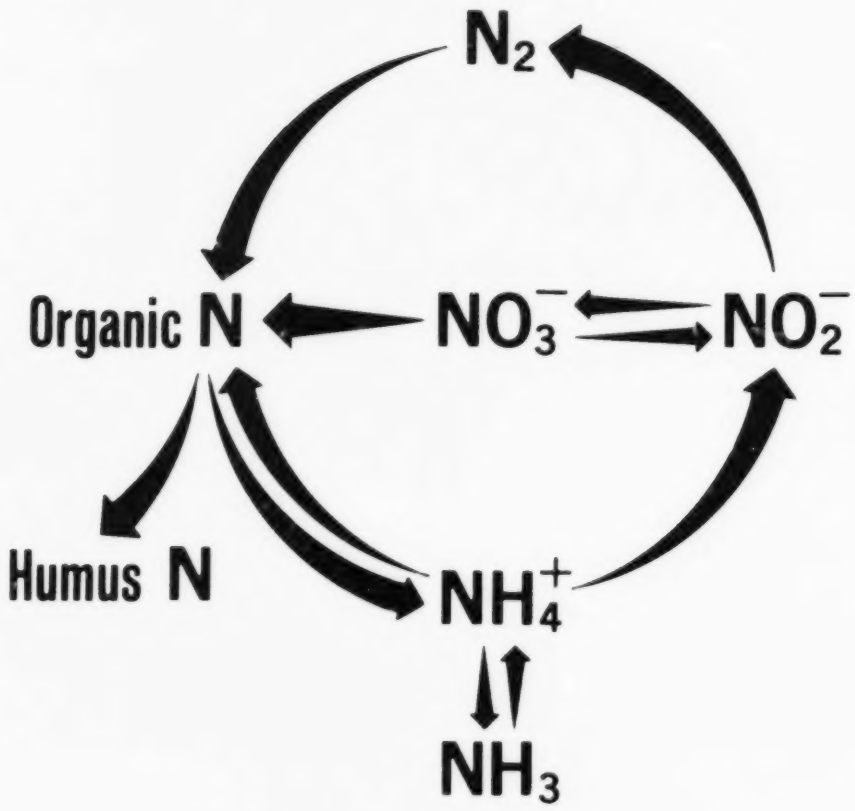
NITROGEN REMOVAL FROM WASTEWATERS



FEDERAL WATER QUALITY ADMINISTRATION
DIVISION OF RESEARCH AND DEVELOPMENT
ADVANCED WASTE TREATMENT RESEARCH LABORATORY
CINCINNATI, OHIO
OCTOBER 1970

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FOREWORD

Classically, sewage treatment has been directed toward the removal of suspended solids, biochemical oxygen demand and reduction of bacterial contaminants. Removal of nutrients such as phosphorus and nitrogen has been incidental to treatment processes. The rapid increase in severe eutrophication problems in recent years has focused attention on nutrient control from municipal sources.

Phosphorus removal techniques, as a result of extensive research over the past several years, are now useable by cities and are awaiting the extensive application that is expected. Nitrogen transformation or removal from most wastewaters will have to be accomplished. In some instances, converting ammonia to nitrates will be sufficient; in other cases, full nitrogen removal will be required.

Full scale treatment plants designed for nitrogen removal are not yet in operation in the United States. A full scale (50 mgd) plant to convert ammonia to nitrate is being designed. Biological denitrification can be designed when needed. The Advanced Waste Treatment Research Laboratory has conducted and sponsored much of the current research on nitrogen removal. This report, assembled by Dr. Robert B. Dean with the assistance of several staff members, provides a state of the knowledge on nitrogen removal that is current as of October 1, 1970. This report supersedes an earlier report dated May, 1970.

F. M. Middleton
Director of Research
Advanced Waste Treatment
Research Laboratory

NITROGEN REMOVAL FROM WASTEWATERS

INDEX

Foreword

Abstract

1.	Nitrogen Removal from Wastewaters--Statement of the Problem	Barth and Dean
2.	Nitrogen Removal by Biological Suspended Growth Reactors	Barth
3.	Nitrogen Removal from Wastewaters by Column Reactors	Smith
4.	Ammonia Nitrogen Removal by Stripping with Air	Farrell
5.	Removal of Ammonia Nitrogen by Selective Ion Exchange	Dean
6.	Ion Exchange for Nitrate Removal	Dobbs
7.	Other Methods for Removing Nitrogen	Dean
8.	Salt Creek Two Stage Nitrification Plant	Woodward

Bibliography

NITROGEN REMOVAL FROM WASTEWATERS

Edited by Robert B. Dean
Advanced Waste Treatment Research Laboratory
Robert A. Taft Water Research Center

ABSTRACT

Ammonia and nitrates are the principal forms of nitrogen in wastewaters. Ammonia is converted to nitrates by biological oxidation. Because of this reaction it exerts a high BOD in surface waters. Nitrates are reduced to nitrogen gas by bacteria when organic matter exceeds the oxygen supply. Both compounds are algal nutrients but ammonia is much more toxic than nitrates. The best developed method for control of nitrogen compounds is biological oxidation to nitrates followed by denitrification with the aid of methanol.

Ammonia stripping at high pH in cooling towers following lime treatment is effective but cannot be used during freezing weather and may suffer from serious scale problems. Selective ion exchange of ammonia with lime regeneration may be practical but the process is still in the pilot stage. Several other processes are being studied. A bibliography of pertinent references is attached.

Paper No. 1

NITROGEN REMOVAL FROM WASTEWATERS -- STATEMENT OF THE PROBLEM

Edwin F. Barth and Robert B. Dean

Nitrogen is continuously cycled through the environment from the atmosphere to growing plants and back to nitrogen gas. The principal species are presented in the classical nitrogen cycle as shown on the cover. Fixation of nitrogen to produce organic nitrogen is carried out by specialized bacteria, algae and a few higher plants. When these organisms decompose much of the organic nitrogen is converted to ammonia. A small fraction however is converted to relatively stable humus nitrogen in the soil. Ammonia and ammonium ion are rapidly interconvertible and the ratio of the two species depends on the pH according to the equation:

1) $\log (NH_3/NH_4) = pH - 9.25$ at 25°

Minor corrections to this equation are necessary in brackish waters and at low or high temperatures. Below pH 7.25 less than 1% of ammonia is present as NH_3.

Ammonia is nitrified or converted to nitrates by two specialized groups of bacteria. Nitrosomonas oxidizes ammonia to nitrite and Nitrobacter oxidizes nitrite to nitrate. Oxygen is required as well as CO_2 for bacterial growth but dissolved organic matter has little or no influence. Nitrifiers are very sensitive to poisoning by many simple substances including heavy metals and free ammonia. Biological nitrification of industrial wastes can therefore not be assumed without careful testing under realistic conditions.

Nitrates can be reduced by many bacteria that use the oxygen for metabolism Nitrites are the first product but they are usually rapidly reduced to nitrogen gas by further bacterial action. Nitrates can also be utilized as a source of nitrogen by most growing plants.

The nitrogen content of natural unpolluted waters is normally less than one milligram per liter, and during the growing season, soluble nitrogen compounds are virtually completely depleted by growing plants and algae (AWWA, 1970).* The presence of nitrogen compounds, particularly ammonia, has therefore been taken as an indication of pollution for over a century. Historically, nitrogen analyses have seniority over BOD_5 and suspended solids determinations to trace wastewater pollution and to control biological treatment. The BOD_5 tests replaced tests for various nitrogen compounds for two reasons. First, analysis was not as tedious; and secondly, the BOD_5 tests made biological processes look more efficient, since it is much easier to get 85% reduction of BOD than it is to get a comparable conversion to nitrates.

Municipal wastewaters have nitrogen contents in the 15-25 mg/l range in untreated and primary settled wastes; the nitrogen is divided between organic compounds, which are mostly insoluble, and ammonia. Biological treatment converts most of the organic nitrogen to ammonia, and under favorable conditions ammonia may be oxidized to nitrates. Nitrogen compounds of lesser significance are discussed in paper No. 7.

The conditions for nitrification of municipal effluents have been worked out by Downing and Hopwood (1964) who showed that

> "to achieve nitrification consistently, the period of aeration must exceed a minimum value which is a function of the concentration of activated sludge, the temperature, and the strength of the sewage. When conditions are favourable for nitrification, the rate of nitrification and the rate of consumption of oxygen due to this process will tend to an equilibrium level which is proportional to the concentration of activated sludge under aeration. In an aeration unit through which the liquid travels with ideal piston-flow, the concentration of ammonia in the effluent under the above conditions will be normally very small. The effect of longitudinal mixing will be to increase slightly the concentration of ammonia in the effluent."

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* All references are collected in the bibliography.

1-3

Biological oxidation of ammonia consumes oxygen and, by definition in Standard Methods, is included as part of the BOD_5 test. However, much of the ammonia demand may not show up in five days because of inadequate seed bacteria or excessive competition from heterotrophic forms. The BOD_{20} is more realistic in assessing the oxygen demand due to ammonia in municipal effluents. The oxygen demand from ammonia in industrial effluents is best calculated assuming complete nitrification.

1) $2NH_3 + 4O_2 \longrightarrow 2HNO_3 + 2H_2O$

According to this equation, 1 mg of ammonia nitrogen could exert an ultimate BOD of 4.5 mg of oxygen. Well over 60% of the biological oxygen demand that will be exerted in receiving waters by biologically treated municipal effluents will be due to oxidation of ammonia to nitrate by the stream's flora. The BOD bottle is a relatively inefficient system for nitrification in comparison with the attached flora on the beds of the stream; therefore, reliance on the 5-day BOD bottle has shifted the burden of satisfying nitrogenous oxygen demand from the treatment plant to the receiving water.

It would be beneficial if waste treatment plants were required to produce nitrified effluent. Ammonia nitrogen in effluent has several undesirable features:

(1) Ammonia consumes dissolved oxygen in the receiving water;
(2) Ammonia reacts with chlorine to form chloramines which are less effective disinfectants than free chlorine;
(3) Ammonia is toxic to fish life;
(4) Ammonia is corrosive to copper fittings;
(5) Ammonia increases the chlorine demand at waterworks downstream.

A nitrified effluent, free of substantial concentrations of ammonia, offers several advantages:

(1) Nitrates will provide oxygen to sludge beds and prevent the formation of septic odors;

(2) Nitrified effluents are more effectively and efficiently disinfected by chlorine treatment;

(3) A nitrified effluent contains less soluble organic matter than the same effluent before nitrification.

In general, we can depend on conventional biological processes to transform almost all nitrogenous components in wastewater into ammonia and biological sludge. Once this has been accomplished, we can design systems to remove ammonia by air-stripping, or we can proceed to a second biological conversion of the ammonia into nitrates. A nitrified effluent may be acceptable for discharge, but if the nitrate level is too high it can be further treated by biological action to convert the nitrates to nitrogen gas.

Ammonia and nitrate are interchangeable nitrogenous nutrients for green plants and algae, as well as bacteria. Some species may prefer ammonia, and others nitrate, but in general they can be considered interchangeable (Flaigg and Reif, 1954). When algae grown on nitrates decompose they will liberate nitrogen in the form of ammonia.

Nitrogen and Eutrophication

The head of the National Eutrophical Program of the FWPCA has stated (Bartsch, 1970),

> "In many lakes that are in trouble because of eutrophication, the nutrients of prime significance are nitrogen and phosphorus. Phosphorus is found to be critical in terms of extensive production more frequently than nitrogen. In some cases it has been demonstrated through field study and appropriate assays that nitrogen does occupy a critical role. Reasons for pessimism relative to nitrogen control (of eutrophication) are the following:
>
> "(1) Many microorganisms can fix atmospheric nitrogen and make it available. Included are bacteria, some of the blue-green algae which are causes of bloom problems, and actinomycetes.

"(2) Nitrogen can pass through the soil and into the ground water and find its way into surface waters more easily than phosphorus. Ammonia can also find its way into surface water via precipitation, in some locations up to as much as 20 lbs/acre per year.

"Situations where nitrogen control must be used for control of eutrophication include the upper San Francisco Bay, where it has been demonstrated that nitrogen is the critical element. There is some thought that lakes that are young in the aging process are more likely to be nitrogen limiting than lakes that have started down the pathway of eutrophication. Lake Tahoe is an example where nitrogen may or may not be a limiting nutrient. In some bodies of water where phosphorus may be limiting part of the time during the growing season, nitrogen may normally be limiting at other times. It is possible to exercise some guided judgment in the matter of limiting nutrients through use of test procedures like the Provisional Algal Assay Procedure (PAAP, 1969)."

Nitrogenous Oxygen Demand

The Chief of the Engineering Section, Chesapeake Technical Support Laboratory, Middle Atlantic Region, FWQA, has stated in regard to nitrogen removal needs (Jaworski, 1970):

"In the upper Potomac Estuary about one half of the dissolved oxygen sag is due to a nitrogenous demand of organic matter being discharged from wastewater effluents in the Washington metropolitan area. During the low-flow summer months, dissolved oxygen levels of less than 2 mg/l in a 10-mile reach are common. Studies by CTSL, FWQA and Maryland Department of Water Resources have established that the dissolved oxygen deficits in the middle portion of the Patuxent River basin are mainly attributable to the nitrogenous demand of organic matter originating from wastewater discharges.

"To eliminate the dissolved oxygen deficit in the Potomac Estuary and in the Patuxent River, the removal of nitrogenous demand is required to manage the water quality in both areas. The State of Maryland has gone on record as requiring a maximum of 1 mg/l of ammonia in effluents discharging into the Patuxent River. To enhance the water quality of the Potomac River basin, the recent Potomac Enforcement Conference required 85% removal of the present nitrogenous oxygen demand from treated waste discharges in the Washington metropolitan area.

Algal Growth Response

"At the present time, predictive generalizations cannot be made for the response of algae to nutrients for all receiving waters. Different geophysical systems appear to be responsive to different limiting nutrients.

"In the Potomac Estuary during summer periods, nitrogen appears to be the rate limiting nutrient at the salinity-freshwater interface. Data from the James River Estuary by VIMS also indicate that the rate limiting nutrient is nitrogen. Thus it appears that nitrogen can be a manageable nutrient with respect to the control of eutrophication.

"If a wastewater system is selected that converts all or most of the nitrogen to nitrates, this will aid the immediate oxygen deficit caused by the oxidation of NH_3 to NO_3. Since NO_3 can be readily converted to organic nitrogen and NH_3 by bacteria and algal cells in waters, the potential nitrogenous demand will still be present. Therefore, carbon and phosphorus as well as nitrogen are the important parameters in the control of eutrophication with respect to the elimination of nuisance algal conditions and the enhancement of water quality.

"While the control of organic carbon and phosphorus will reduce the incidence of algal blooms, the addition of nitrogen removal will further enhance the control of the blooms. If wastewater treatment processes are added to convert the nitrogen to NO_3 without considering the complete removal of nitrogen, we are just transporting the problem farther downstream."

The State of Illinois has recently set an effluent standard of 2.5 mg/l of ammonia (2.05 mg/l ammonia-N) for discharge to surface waters. A substantial fraction of the oxygen sag in the Grand and Clinton Rivers in Michigan and in the Kanawha River, West Virginia, below a large industrial complex, has been attributed to the BOD of ammonia. It was early practice in Britain to nitrify effluents as evidence of good biological treatment since nitrification is difficult in the presence of large amounts of readily decomposable organic matter. Furthermore, nitrates in the water provide oxygen to help oxidize organic matter present from other sources, and to prevent septicity. Nitrates, usually as chili saltpeter, have frequently been used to control septic odors in estuaries and lagoons (Lang, 1966).

A review article of British water pollution control (Jenkins, 1970) states that a recent requirement limits ammonia nitrogen in sewage effluents not to exceed 10 mg/l. This means that a treatment plant must be designed to give complete purification to three times the dry weather sewage flow and that 60% to 70% of the ammonia nitrogen must be oxidized at all times. River control agencies regard nitrification as desirable because of the high oxygen demand of ammonia nitrogen, the toxicity of ammonia to fish under certain circumstances, the reduction in chlorine demand, and the oxygen reserve present in nitrates.

Ammonia standards for several states were reviewed by Battelle Northwest (1969).

Ammonia is rapidly adsorbed by soil minerals and particulate matter containing nitrogen is also effectively removed in the soil. However, if there is not sufficient plant growth in the soil to use the bound ammonia, it will be converted to nitrates by nitrifying bacteria. Nitrates are very poorly adsorbed in the soil, and rapidly reach the ground water when present in excess. Therefore, over-fertilization with nitrogen compounds, whether they be ammonia, slow-release nitrogen, or nitrates, can lead to high concentrations of nitrates in ground water.

Ammonia has very little toxicity to humans and there are no limits on ammonia in the USPHS Drinking Water Standards of 1962, or the WHO International Standards. Ammonium compounds have been used in cooking and ammonia gas is the essential ingredient of smelling salts. Various suggested limits on ammonia in drinking water are related to the fact that ammonia is generally taken as an indicator of fecal pollution and the fact that high levels of ammonia dissolve copper from plumbing. The toxicity of ammonia to fish and other aquatic species is much higher than for humans, but details have not been completely elucidated. According to many references, the toxicity of ammonia and ammonium salts to aquatic animals is directly related to the amount of undissociated ammonium hydroxide in the solution, which in turn is a function of pH. Toxicity has been reported at levels as low as 0.2 mg/l of undissociated ammonia nitrogen (McKee and Wolf, 1963).

Nitrates have low toxicity for plants and animals. Saltpeter (potassium nitrate) has traditionally been used as a curing agent for ham. Nitrates in food and water are normally denitrified by bacteria in the intestines. However, some very young babies do not have a complete intestinal flora. The bacteria which are present reduce nitrates to nitrites, and do not carry the reduction further to nitrogen gas. Nitrites combine with hemoglobin to produce methemoglobinemia, a disease characterized by

cyanosis. PHS and WHO standards recommend not more than 10 mg/l of nitrate nitrogen (45 mg/l nitrate) for water to be fed to babies. Many well waters contain more than 10 mg/l of nitrate nitrogen, and particularly among poorer classes and migrant laborers it is very difficult to make sure that babies are not given this water.

The following papers discuss specific processes which can be used to remove nitrogen compounds from water.

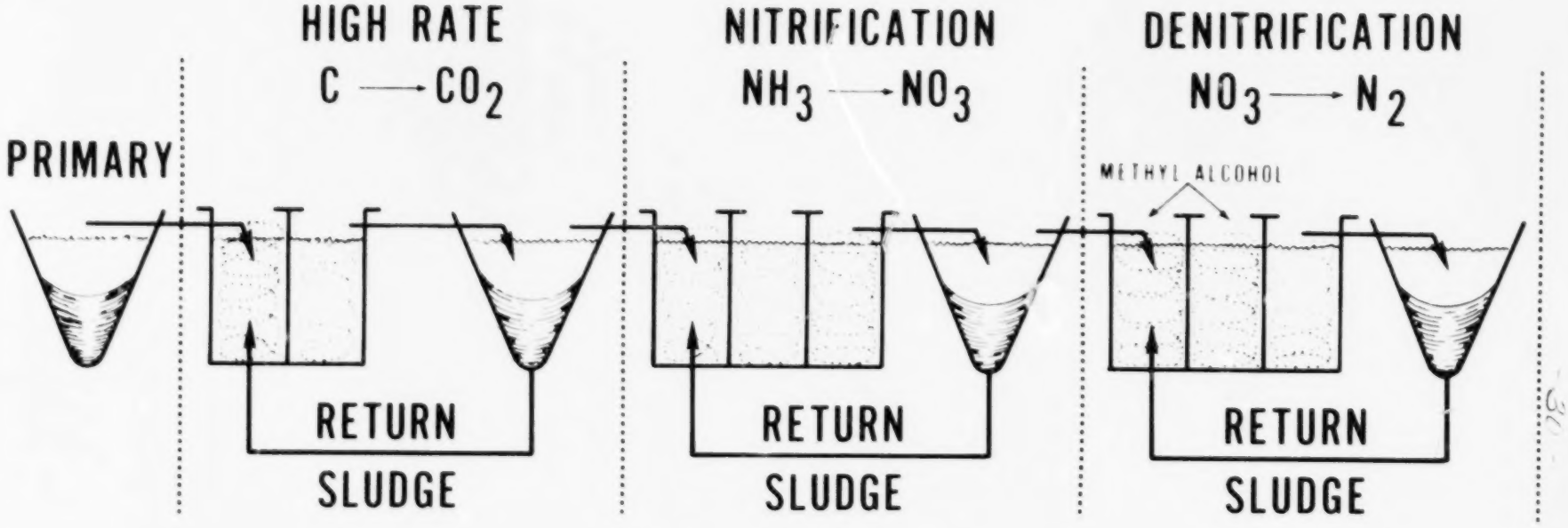

FIGURE 1

THREE SLUDGE SYSTEM FOR NITROGEN REMOVAL

Paper No. 2

NITROGEN REMOVAL BY BIOLOGICAL SUSPENDED GROWTH REACTORS

E. F. Barth

Other sections of this report deal with chemical and physical processes to remove nitrogenous components of wastewater. While these are being actively investigated, our basic capability resides in carefully managed biological systems. Success in providing a high efficiency for nitrogen removal by biological denitrification requires that the biological transformation of ammonia nitrogen to nitrate nitrogen be under good process control. Any reduced nitrogen compounds introduced into the denitrification stage will pass through the process unaltered and impair overall nitrogen removal efficiency.

Downing and Hopwood (1964) revealed the complex factors involved in maintaining nitrification with a conventional activated sludge system. A three sludge variation of the activated sludge process has been developed which greatly simplifies the process control problems associated with maintaining nitrification (Barth, et al., 1968). Figure 1 is a schematic of the process developed for nitrogen removal by biological denitrification. Figure 2 is a representation of a municipal application of the three sludge system taking advantage of common wall construction techniques for economy in construction.

The three sludge system allows management of the separate biological transformations which are necessary for successful denitrification. As shown on Figure 1 the high rate system handles the bulk of the carbonaceous removal and at this station the waste activated sludge is removed. Thus, the nitrification stage receives a predominantly ammonia nitrogen feed and an enriched culture develops because each system has its own sludge recycle. This process design also has other desirable features. The high rate system protects subsequent nitrification stages from toxic chemicals. Heavy metals, cyanides, thiocyanates, and toxic organic chemicals will be either sorbed or biologically degraded before they reach the nitrification stage. Since this is a staged system there can be no direct short circuiting of materials from the influent to the effluent. Temperature effects on the enriched culture of the nitrification stage are not as extreme as

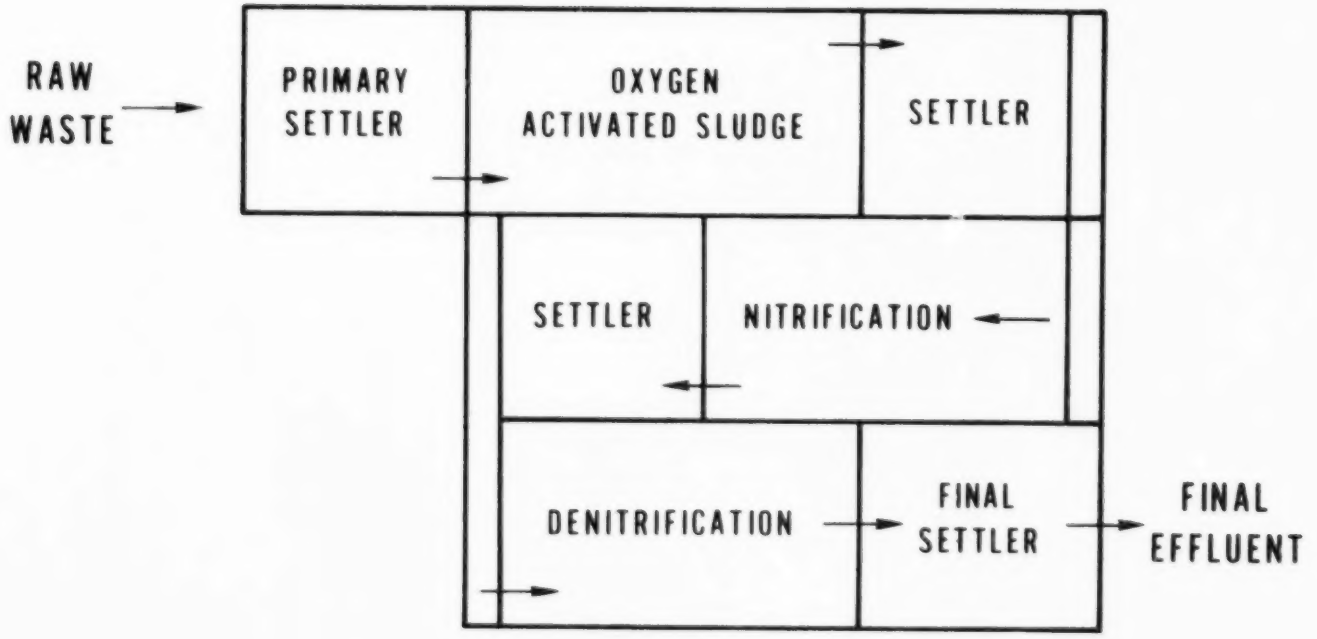

FIGURE 2

COMMON WALL CONSTRUCTION OF 3-SLUDGE SYSTEM

with a single sludge system which contains only a marginal population of nitrifying organisms.

Once controlled nitrification has been established the biological denitrification process can be optimized. The nitrified effluent flows to a stirred anaerobic reactor where methyl alcohol is added in proportion to the nitrate nitrogen concentration. The organisms in this stage use the oxygen component of the nitrate radical to oxidize the organic carbon of methyl alcohol. The end products of this metabolism are elemental inert nitrogen gas and carbon dioxide, which are liberated to the atmosphere.

The stage approach to nitrification has been investigated through grant and contract activities and work at the Robert A. Taft Water Research Laboratory. Large pilot plant operations are located at the University of Notre Dame and Manassas, Virginia. The process has also been evaluated at a 1 MGD scale at Hazel Crest, Illinois. Temperatures as low as 6° C have been recorded, with no detrimental effect on nitrification. Previous experience with the stage approach to nitrification has been reported by English and South African investigators (Osborn, 1965).

Biological denitrification has been studied by microbiologists for many years, particularly in regard to loss of nitrogen from soils (van Schreven, 1963). There have been intensive recent studies related to the application of denitrification to wastewaters. Wuhrman (1960) and Bringmann and Kuhn (1965) have both published in Europe. American experience includes studies at the Robert A. Taft Water Research Laboratory (Barth, et al., 1968); the Lebanon Plant, Firebaugh, California (McCarty, et al., 1969); Notre Dame, Indiana (Echelberger and Tenney, 1969); Manassas, Virginia (Mulbarger, et al., 1969); and Pomona, California (Carey, 1968). A summation of these studies show that biological denitrification is a controllable process if the reaction is forced with an organic supplement, such as methyl alcohol. Attempts to use waste organic matter from sewage have been less successful.

Packed column processes as well as suspended growth reactors have given efficient nitrogen removal. Large scale municipal application, in the range of 2 MGD or greater would favor suspended growth reactors. The 300 MGD Blue Plains Washington, D. C. municipal facility tentatively is

being designed on the basis of a three-stage biological system for both nitrogen and phosphorus removal after an extensive review of both chemical-physical approaches and biological approaches to nitrogen removal.

The Blue Plains plant will employ a final filtration step to assure quality control of the effluent. Filtration of effluents is necessary for high efficiency whether we are considering suspended solids, chemical oxygen demand, nitrogen, or phosphorus. We must have positive control of the solids no matter what treatment process we employ.

Figure 2 showing the municipal application of this process indicates that the current technology development of high purity oxygen for carbonaceous removal can be combined with this staged system to give very reasonable detention times. A two hour oxygen aeration period combined with one hour detention in each of the settlers, and two hours each for nitrification and denitrification give a total flow through time of ten hours.

The three-stage biological system can produce an effluent containing 2 mg/l, or less, of total nitrogen. This is a very realistic figure to use as an effluent standard, and when dealing with municipal wastewaters it represents 90 percent or greater removal of total nitrogenous materials.

The capital cost of such a system would be about 25 percent more than a conventionally designed activated sludge process of equal flow. The use of high purity oxygen in the first and second stages could bring the capital cost almost exactly in line with conventional capital costs.

The operating cost for the methyl alcohol to supplement the denitrification process is 1.6 cents per thousand gallons for a wastewater containing 20 mg/l of nitrogenous material.

Paper No. 3

NITROGEN REMOVAL FROM WASTEWATERS BY COLUMN REACTORS

J. M. Smith

Once nitrates are formed in sewage treatment they can be converted to nitrogen gas by the action of microbes and a source of BOD. Columnar nitrate reduction represents an alternate to the suspended growth systems as a means of biochemically reducing the nitrate ion to elemental nitrogen (see Figure 3). A variety of facultative bacteria common in wastewater including the genera Pseudomonas, Achromobacter and Bacillus are known denitrifiers. When supplied with a suitable organic carbon source under anaerobic or near anaerobic conditions these organisms use nitrates and nitrites as the terminal hydrogen acceptors during the fermentation of the added substrate to ultimately form nitrogen gas.

In a packed column the cell residence time of the surface bound slime is much greater than the hydraulic detention time. This, combined with a large contact surface and short diffusion distances afforded by small media such as sand, provides an efficient system for rapid denitrification of an applied feed.

Work at Lebanon, Ohio (J. M. Smith, 1970, Unpublished) has shown that the smaller media systems (sand to 3/4 inch diameter stone) are effective when operated downflow at surface loading rates of 7.0 gpm/ft^2 and at actual contact times of 5 to 30 minutes. The downflow operation, using either granular carbon or sand, requires daily backwashing using 1-3 percent of the throughput stream to relieve pressure drop due to the accumulation of suspended solids in the upper portion of the column. The denitrifying slime is firmly attached to the media surface, and is not removed during the backwash operation. Greater than 90 percent nitrate reduction can be achieved within these columns at contact times of 10 minutes for sand and 30 minutes for the 3/4 inch stone. The effluent normally contains less than 2.0 mg/l of nitrate nitrogen with effluent turbidities less than 3 JTU, indicating little solids contribution from the attached organisms. The ammonia and organic nitrogen content of the feed is not significantly changed during the denitrification process.

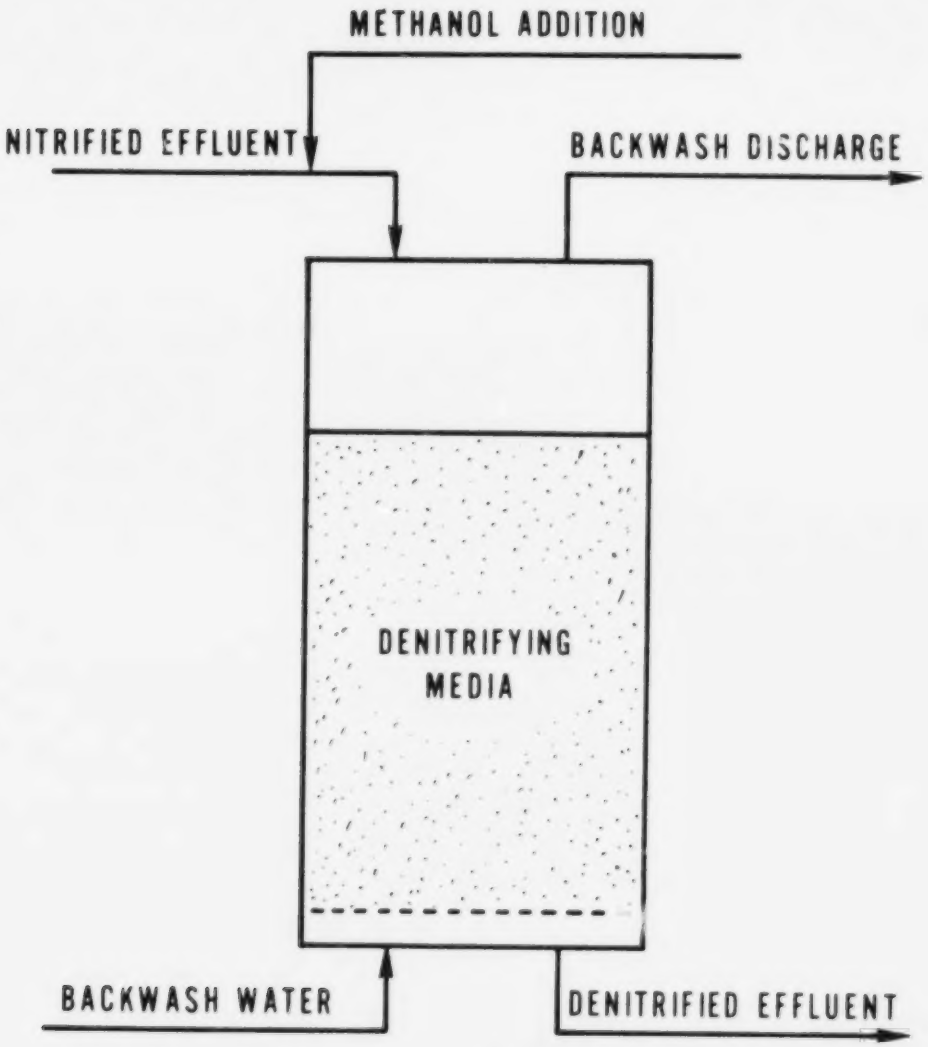

FIGURE 3

PACKED BED DENITRIFICATION REACTOR

Larger media varying in size from 1 inch to 2 inch aggregate has been successfully employed to denitrify agriculture subsurface drainage (Tamblyn and Sword, 1969). The larger media permits upflow operation without backwashing at the expense of longer contact times and increased effluent suspended solids. Nitrate reduction of greater than 90 percent can be achieved in contact times of 1 hour for the 1 inch aggregate and 2 hours for the 2 inch aggregate at temperatures above 12° C. The 2 inch columns have been operated continuously for over six months on agriculture subsurface drainage without the loss of efficiency or solids accumulation.

Methanol is used as the supplemental organic carbon source of choice for denitrification because of its low cost, biodegradability and ease of handling. Approximately 3 mg of methanol are required per mg of NO_3-N removed including the requirement for deoxygenating the nitrified feed. The chemical cost for removing 20 mg/l of NO_3-N in the presence of 5 mg/l of dissolved oxygen is estimated to be 1.6¢/1000 gal.

While the packed bed provides an efficient contacting system for denitrification, total nitrogen removal via biological nitrification-denitrification will depend on the combined efficiency of the nitrification stage as well as the denitrification stage. This interdependence of two biological systems will limit total nitrogen removal efficiencies to a practical value of about 90 percent.

Pilot plant experiences to date firmly support a full scale demonstration of columnar nitrate reduction at the 1 MGD level or above. One possibility is the construction of a new facility that incorporates a two stage nitrifying system followed by columnar denitrification. An alternate, and equally plausible idea is to modify an existing conventional activated sludge process by splitting the aeration tanks into a two sludge system by the addition of a second settler, perhaps a tube settler, followed by denitrification on a relatively fine media that will also serve as a solids polishing process. The design of a denitrification system is straightforward and involves basic principles of biological oxidation and filtration. When furnished with basic denitrification data any competent sanitary engineering firm should be able to successfully design a treatment plant capable of removing nitrogen.

St. Armant and McCarty (1969) have demonstrated the use of anaerobic filters for removal of nitrates from irrigation return flow collected in drain tiles. They found that methanol requirements were close to the theoretical. The most satisfactory media was one inch diameter gravel operated upflow. Detention times of one hour were satisfactory at temperatures above 12°C. The treated water contained less than 1 mg/l nitrate and slightly more nitrite. It had no dissolved oxygen. Sludge production by the denitrifying organisms produced turbidity which would have to be removed by filtration.

Paper No. 4

AMMONIA NITROGEN REMOVAL BY STRIPPING WITH AIR

J. B. Farrell

Ammonia is a gas which dissolves in water to an extent controlled by the partial pressure of the ammonia above the water. An increase in its partial pressure causes more ammonia to dissolve, reducing its partial pressure causes ammonia to leave the water phase and enter the gas phase. If it is desired to remove ammonia from water, this can be done by contacting the water with a sufficient quantity of ammonia-free air. This physical process is called desorption or, more commonly, "stripping."

Wastewater contains the ammonium ion at concentrations which typically range from 15 to 25 mg/l. If the ammonium ion is converted to dissolved ammonia by raising the pH, the ammonia may be stripped out by contacting the wastewater with air. Early studies of feasibility of stripping of ammonia from wastewater (Kuhn, 1956) showed a major difficulty: the volume of air per unit volume of water is very high, about 400 cubic feet per gallon of water in a countercurrent-flow packed tower. The pressure drop across a packed tower is about 1.0 psi or 28" of water. Since power is proportional to the product of volumetric flow rate and pressure drop, the cost for power made the process prohibitive even at this relatively low pressure drop.

The problem of high power cost was solved by investigators at the South Lake Tahoe Public Utility District (Slechta and Culp, 1967) who used a slat-filled tower such as is used for cooling water to contact water and air. The pressure drop across such a device is very low--about 1/2 inch of water--so power costs are reduced to reasonable levels. Removal efficiencies as high as 90 percent were obtained in a 24-foot high tower in which water and gas were contacted in a nearly countercurrent fashion. On the basis of this experience, a full scale stripping tower was constructed at South Lake Tahoe. The tower was designed to remove 90 percent of the ammonia from 3-1/2 MGD of Tahoe's renovated wastewater. The air flow is not countercurrent to the water but flows across the tower (cross-flow), while the water drips downward through the packing.

Initial operation of Tahoe's stripping tower was in the winter and immediately revealed a limitation of ammonia stripping. The cold air contacting the wastewater quickly cooled the water. Ammonia solubility is higher in cold water than in warmer water; consequently, more air is required to remove it. For example, at 0° C it would take about 800 cubic feet of air per gallon of water to remove 90 percent of the ammonia from wastewater in a countercurrent tower. Since the Tahoe tower was designed for 400 cubic feet per gallon, percent removal was much lower than 90 percent. When air temperature fell below 0°, freezing of water occurred at the air inlets, making the tower inoperable. From theoretical considerations, difficulty with freezing may be anticipated when the wet-bulb temperature of the ambient air is below 0° C.

Another problem which developed at Tahoe is the formation of scale in the tower. The scale is chiefly calcium carbonate. It forms because the previously lime-treated effluent is supersaturated with respect to calcium carbonate. A more important reason is the presence of carbon dioxide in the air. A small portion of the carbon dioxide reacts with the basic wastewater, forming calcium carbonate which precipitates. In the case of the tower at Tahoe, the sludge can be flushed from the tower except from inaccessible areas which cannot be reached with a water jet. A pilot plant ammonia stripping tower at Blue Plains, Washington, D. C., had similar scaling problems, except the scale is hard and adheres to the tower fill. They have been able to get a soft scale by reducing the pH to 10. A pilot tower in New England had similar hard scale (Sawyer, 1970). However, a pilot plant tower has been run in South Africa (van Vuuren, 1970), and here the scale has been so soft that the force of the water dripping through the tower fill has been sufficient to flush out the scale.

The causes of the differences in the nature and amount of scale in various locations has not been resolved. Some suggested factors influencing the nature of the scale are: type of contact (countercurrent or cross-flow), recirculation of sludge, pH of the wastewater, and chemical makeup of the wastewater. Studies are in progress to see if the scale can be prevented from forming, or if it can be made nonadherent.

The cost of ammonia stripping has been estimated by Suhr (1969) for South Lake Tahoe facility to be about 2.9¢ per 1000 gallons of wastewater treated. This does not include the cost of the lime and facilities to raise the pH to about 11. These costs have been charged to phosphorus removal because this is the direct objective of the lime addition. If 90% removal of ammonia nitrogen is required even in cold weather, these costs should be increased by about 50% to provide for a higher air-to-water ratio. In below-freezing weather the tower will be inoperable. It is possible to heat the incoming air to temperatures above 0° C and add moisture to it to prevent freezing. This procedure would only be economical if subfreezing days are rarely encountered.

Methods for designing ammonia stripping towers have been developed at the Taft Center by Roesler et al. (1970) but have not yet appeared in the literature. Ammonia stripping is feasible when the temperature is above freezing but there is danger of serious fouling by scale. The best approach for minimizing scale and its effects appears to be to use a pH of about 10.5, countercurrent operation rather than cross-flow, and an open fill to allow for easy flushing of accumulated solids.

Paper No. 5

REMOVAL OF AMMONIA NITROGEN BY SELECTIVE ION EXCHANGE

R. B. Dean

Ammonia exists in solution predominantly as the ammonium cation (NH_4^+) unless the pH is higher than about 9.5. The ammonium ion is very similar to the potassium ion in size and is precipitated by the same reagents that precipitate potassium. Adsorption of ammonium ion on ion exchange resins is ordinarily very similar to the adsorption of potassium or sodium ions. Therefore, conventional water softening ion exchange resins which are selective for calcium and magnesium do a relatively poor job of removing ammonium from dilute solutions. Total deionization by mixed bed ion exchange resins will, of course, remove ammonium ions along with other cations but this process is too costly for wastewater treatment.

Certain zeolites show unusual selectivity for the ammonium ion. A number of these have been investigated by the Atomic Energy Commission because they also show selectivity for cesium and potassium ions. A demonstration project at the Battelle Memorial Institute - Pacific Northwest (Hanford) Laboratories, 1969 (see Mercer, 1970), showed that certain zeolites, including the naturally occuring mineral clinoptilolite, had a high selectivity for ammonium in natural and wastewaters. A trailer mounted demonstration plant with a capacity of 100,000 gallons per day was built as a cooperative demonstration project between the FWQA and Battelle-Northwest. This trailer is now operated under contract to the FWQA to demonstrate selective ion exchange removal of ammonium ions from solution.

Preliminary work demonstrated that native clinoptilolite from Hector, California, could be used after grinding and sieving to 20 x 50 mesh. When columns filled with this material were fed secondary effluent they clogged rapidly; therefore, the trailer incorporates an inclined-tube settler clarifier to remove turbidity from the feed. Clarified water is treated by conventional downflow through two columns in series. When ammonia breaks through the second column, the first column is taken offstream and a third column containing freshly regenerated clinoptilolite is added after the second column which now becomes the first in the series. The loaded column is regenerated by backwashing with limewater containing sodium chloride to

speed up the rate of regeneration. The concentration of sodium chloride is approximately that which will be reached after several regeneration cycles. The high pH of the limewater converts the ammonium ion to unionized ammonia gas in solution. This is allowed to build up to a level of about 500 mg/l by recycling of the limewater. Precipitates such as magnesium hydroxide which may form in some hard waters are removed by settling.

The ammonia laden limewater is then pumped through a packed column through which heated air is blown to remove the ammonia. The problems of ammonia dispersal to the atmosphere are similar to those encountered in direct air stripping of ammonia. However, the ammonia content of the gas stream is 20 to 50 times as strong as occurs with direct air stripping and there is proportionately much less air to be heated in cold weather. On a large scale it would probably be more economical to use stripping towers of the cooling tower type rather than packed towers because the latter have very high pressure drops. However, a packed tower is much more compact and could be incorporated in the available space on the trailer.

Because of the high concentration of ammonia, its odor is readily detectable in the effluent gases. Of course, the total amount of ammonia vented to the atmosphere is the same whether ammonia is stripped directly or is first concentrated in an ion exchange column. Direct stripping of ammonia from municipal effluents would produce a concentration of ammonia nitrogen in the air of approximately 0.03 ppm, which is well below the threshold for detection by odor.

Ammonia in the atmosphere reacts with sulfur dioxide which is present in large excess over all cities. If all of the ammonia present in sewage in the United States were to be discharged to the atmosphere, it would be equivalent to less than 10 percent of the sulfur dioxide being discharged to the atmosphere. Ammonia and SO_2 together can cause fog under some conditions; however, unneutralized sulfur dioxide eventually forms sulfuric acid which is even more objectionable. Further studies on the behavior of ammonia in urban atmospheres are warranted (Miner, 1969).

Ammonia gas in the atmosphere, whether or not it reacts with sulfur oxides, is adsorbed by moisture in soil, vegetation, and open water

surfaces. That portion which goes into the soil and vegetation will be bound and will no longer be a pollutant. However, if prevailing winds would blow ammonia laden air over inland bodies of water, as for example at Toledo, then ammonia stripping to protect surface waters would not be appropriate.

The cost of removing ammonia by ion exchange has been estimated by Eliassen as 8.1¢/1000 gallons. His estimate includes the cost of brine for regeneration but does not include the cost of disposal of the ammonia laden brine. In most areas this could be a serious problem since discharge to surface waters would be self-defeating. Pilot studies at Battelle-Northwest indicated a cost of between 3 and 6¢/1000 gallons for their Zeolite method. An estimate prepared for a 7.5 MGD plant at Lake Tahoe showed 15¢/1000 gallons which is probably high. By comparison with other fixed bed adsorption methods it is reasonable to suggest a cost of about 10¢/1000 gallons for ammonia removal by zeolites. More reliable cost estimates will be available at the conclusion of present pilot plant studies. Alternative methods of regenerating zeolites which convert the ammonia to nitrogen gas are also being investigated.

Paper No. 6

ION EXCHANGE FOR NITRATE REMOVAL

R. A. Dobbs

Ion exchange is a standard unit process in the water treatment field. Large units have been installed for softening municipal water supplies. The resins used are fairly selective for the divalent cations of calcium and magnesium which are responsible for most of the hardness in water. Unfortunately, a comparable resin with a high selectivity for nitrate ion over other anions does not exist.

A technical and economic evaluation of the feasibility of removing nitrate from irrigation return drain water has been made by the Dow Chemical Company (1968). Although the concentration of anions in the drain water is considerably higher than the corresponding concentration in wastewater, the ratio of nitrate to chloride is quite similar for both waters. Several conclusions related to the drain water can be extrapolated to municipal wastewater. Commercially available anion exchange resins have a selectivity for nitrate over chloride. In order to develop an economic process this selectivity ratio should be approximately 20.

Even if resins of the required selectivity could be developed, additional problems must be solved in order to make the process practical. Regeneration of selective ion exchange resins are usually difficult. Based on the nitrate anion alone, efficiency of sodium chloride regeneration is of the order of 1%. Another serious problem involves the ultimate disposal of the nitrate laden brine produced during regeneration. Theoretically, resin regeneration could be achieved with sodium sulfate. Nitrate could be reduced chemically with ferrous sulfate and neutralized with lime to produce sludges and nitrogen gas as discussed in the next section. However, chemical and sludge disposal costs are likely to make the process uneconomical. In the brine regeneration process the high concentration (15%) of salt suggests the possibility of electrochemical treatment of the regenerant to produce nitrogen gas and chlorine.

Several attempts have been made to develop selective ion-exchange processes for nitrate removal. Dow Chemical Company is presently under contract (Contract No. 14-12-808) to develop a nitrate removal process based on the use of a porous solid absorbent containing a nitrate-selective

water-immiscible extractant. The process has the advantages of liquid ion-exchange technology and the ease of operation of the granular bead resin systems.

Selective nitrate removal by ion exchange will not be feasible until new resins are synthesized with a high selectivity for nitrate over other anions present in the water. In addition, a suitable process for treating the nitrate laden regenerants must be developed.

Paper No. 7

OTHER METHODS FOR REMOVING NITROGEN

R. B. Dean

In addition to ammonia, nitrites and nitrates already discussed, nitrogen can occur in wastewaters in several other forms. Small concentrations of amino acids are leached from bacteria under anaerobic conditions. Digester supernatants contain a relatively high concentration of soluble amino acids and secondary clarifiers may release substantial quantities of amino acids if anaerobic conditions are approached in the return sludge. Amino acids are readily biodegraded and are removed in part by lime precipitation and carbon columns. Nitrilotriacetic acid (NTA) has been proposed as a detergent additive to chelate calcium ions as a partial replacement for phosphates. NTA is biodegraded in a well-operated secondary treatment plant. (Bunch and Ettinger, 1967) It is not removed by precipitation with aluminum hydroxide. The behavior of NTA toward precipitation by lime or iron salts and its behavior in the column of activated carbon containing adsorbed organic matter and a bacterial flora are now being studied at Cincinnati. NTA levels in wastewater are not expected to exceed about 2 mg/l as nitrogen.

Urea is the principal form in which nitrogen is excreted. Fortunately, urea is rapidly hydrolyzed to ammonia by bacteria in sewer lines and biological treatment plants. In the absence of biological action it would be extremely difficult to precipitate or adsorb urea from solution. Organic nitrogen is also present in particulate form both in raw sewage and in secondary effluents. In the latter case bacteria and bacterial fragments account for nearly all the suspended nitrogen. Efficient clarification and filtration are effective ways of removing this form of nitrogen. Typically, the organic nitrogen in the product from a carbon column following secondary treatment is approximately 1.0 mg N/l. This residue has not been characterized but it may be derived from bacterial action.

Soluble nitrogen compounds, with the exception of urea, are ionized in water and 85-90 percent of them can be removed by any deionizing or desalting process such as reverse osmosis, electrodialysis, ion exchange or distillation. None of these processes have a favorable selectivity for ammonium or nitrate ions and it is, therefore, necessary to remove about

90 percent of the salts in order to remove 90 percent of the soluble nitrogen compounds. Distillation is particularly unfavorable since it tends to concentrate ammonia in the distillate unless the feed is kept highly acidic. In that case, nitrous acid will be selectively distilled over (O'Connor et al., 1967). All of the general salt removal techniques are of interest only for water that is to be reused and are too expensive for consideration as treatments for wastes to be discharged to surface waters.

Chlorination of Ammonia. Ammonia reacts with chlorine stepwise according to the following equations:

(1) $Cl_2 + NH_3 \longrightarrow HCl + NH_2Cl$, monochloramine

(2) $Cl_2 + NH_2Cl \longrightarrow HCl + NHCl_2$, dichloramine

(3) $Cl_2 + NHCl_2 \longrightarrow HCl + NCl_3$, trichloramine

Monochloramine is rapidly decomposed to NH_3 and HCl by active carbon. The theoretical breakpoint equation is:

(4) $3\ Cl_2 + 2NH_3 \longrightarrow N_2 + 6HCl$

Actually 4 Cl_2 per $2NH_3$ or 10 mg of chlorine per mg of ammonia nitrogen is required. This means that some higher oxides of nitrogen must be produced in the reaction. A large number of possible compounds may be formed but unfortunately it is difficult to identify them analytically without very sophisticated procedures. Four moles of chlorine per mole of N_2 corresponds to 10 parts of chlorine for each part of ammonia nitrogen. The per capita excretion of ammonia nitrogen is of the order of 10 lbs. per year, equivalent to 100 lbs. of chlorine. A city of 200,000 would, therefore, require about 20 million lbs. or 10,000 tons of chlorine each year. Transport and handling of this amount of chlorine would be hazardous. Also, the use of chlorine would produce an equivalent weight of hydrochloric acid, which would exceed the buffer capacity of most waste waters, and would produce the highly odorous NCl_3. While hydrochloric acid would be effectively neutralized by discharge into the ocean and most surface waters, it could be a serious pollutant and discharge

pipes would have to be made of special acid resistant materials. Sodium or calcium hypochlorite can be substituted for chlorine in equations (1-4).

$$(5)\quad 3NaOCl + 2NH_3 \longrightarrow N_2 + NaCl + 3H_2O$$

No excess hydrochloric acid is produced by the use of sodium hypochlorite, but again it will be necessary to use four moles of hypochlorite per mole of nitrogen or equivalent. Hypochlorite is more expensive than chlorine but is so much safer to use that New York City, Chicago, and other large cities have converted to aqueous hypochlorite for chlorination of water and treated wastes.

Chlorine is manufactured electrolytically according to equation (3):

$$(6)\quad 2NaCl + 2H_2O \longrightarrow H_2 + Cl_2 + 2NaOH$$

Sodium hypochlorite is made by the reaction of chlorine and NaOH. If this is done in the electrolytic cell, equation (4) results.

$$(7)\quad NaCl + H_2O \longrightarrow H_2 + NaOCl$$

Electrochemical production of chlorine or sodium hypochlorite has been practiced for sewage chlorination and treatment for years (Marson, 1967). It has never been optimized. Some source of brine is necessary to raise the conductivity of the water; therefore, electrochemical production of chlorine or hypochlorite has only been attractive for seacoast communities. Breakpoint chlorine treatment, of course, also disinfects as well as destroys ammonia. However, the addition of 200-300 mg/l of chloride might not be acceptable in inland waters.

Just as ammonia can be oxidized to nitrogen, so can nitrate be reduced to nitrogen. In acid media, nitrous acid derived from nitrites reacts with ammonia and amines to liberate nitrogen gas.

$$(8)\quad HNO_2 + RNH_2 \longrightarrow ROH + N_2 + H_2O$$

This reaction, called the Van Slyke reaction, does not proceed in neutral waters. (Brezonik and Lee, 1966) Chemical reduction of nitrates in dilute solution has been accomplished using ferrous sulfate to produce nitrogen gas and some nitrous oxide, N_2O. (Gunderloy et al., 1968) The by-product is a voluminous sludge of ferrous-ferric hydroxide. Some of the sulfate is incorporated in the precipitate but a large part of the sulfate remains in the waste. This process is being studied under contract and at present appears to have marginal value for special situations.

Costs of any of the processes discussed in this section are probably higher than costs for the more promising processes. The only cost that can be calculated direct with some confidence is the cost for chlorine to oxidize ammonia. Assuming 20 parts of ammonia nitrogen in a secondary effluent, 200 parts of chlorine would be required for breakpoint chlorination. This is equivalent to 1.5 lbs. of chlorine per 1000 gallons or about 6¢/1000 gal. To this must be added the cost of handling the corrosive hydrochloric acid produced. Sodium hypochlorite may cost twice as much as chlorine but associated costs are greatly reduced. The cost of electrically generated chlorine or hypochlorite will depend on the cost of electrodes and the possibility of using low-cost off-peak power.

SALT CREEK TWO STAGE NITRIFICATION PLANT
METROPOLITAN SANITARY DISTRICT OF GREATER CHICAGO

by

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The proposed Salt Creek Water Reclamation plant of the Metropolitan Sanitary District of Greater Chicago will serve an area of some 49 square miles in the northwestern part of Cook County about 20 to 25 miles northwest of downtown Chicago. It is primarily a residential area with some light industry. A portion of the area is served by combined sewers. At present, the area is tributary to the North Side or West-Southwest treatment plants but because of the rapid growth of this portion of metropolitan Chicago a decision was reached following a 1965 study by Greeley and Hansen to construct several treatment plants to serve the area rather than to build relief interceptors and to expand the existing plants.

Salt Creek is a tributary of the Des Plaines River. It rises in northwestern Cook County and flows across the northeastern part of Du Page County before reentering Cook County and joining the Des Plaines River. The outfall sewer from the Salt Creek treatment plant will discharge to Salt Creek a short distance above the Cook-Du Page county line and a short distance downstream from a proposed reservoir which is to be built in the Ned Brown Forest Preserve. During the summer months there will be virtually no dilution available for the effluent from the treatment plant. Through much of its length Salt Creek flows through park and forest preserve lands which are used for recreation by large numbers of people. Although the stream is not used to any appreciable extent for body contact recreation it is important that it be maintained as an attractive part of the landscape.

The Illinois Sanitary Water Board has established water quality standards and effluent standards which require an effluent of quite high quality from the Salt Creek plant. Some of the most pertinent of these are:

	Standards	Influent Wastewater
BOD	4 mg/l	95 mg/l
Suspended Solids	5 mg/l	188 mg/l
Ammonia Nitrogen	2.5 mg/l	20 mg/l
Nitrate Nitrogen	45 mg/l	--
Fecal Coliforms	2,000 per 100 ml	--

There is not at present any effluent or stream standard for phosphates in this area.

The wastewater to be treated at the Salt Creek plant is comparatively dilute. A sampling program of one week's duration of the principal sewer which will be tributary to the plant showed the average characteristics summarized in the table.

Treatment Processes Considered

The high effluent quality demanded requires that the treatment process remove most of the carbonaceous and nitrogenous oxygen demanding materials. The two principal processes which had been developed at the time of our studies (late 1967) for removing ammonia were air stripping, which had been studied at Lake Tahoe and nitrification which had been studied by a great many investigators.

Ammonia stripping was considered but was found to be more costly and less reliable than nitrification. The high alkalinity and hardness of this wastewater would have required very large quantities of lime and produced correspondingly large quantities of sludge to be processed. At the low temperatures which prevail in the Chicago area in the winter the process would be quite inefficient in ammonia removal and would probably have to be discontinued because of icing and other operating difficulties.

The nitrification process in activated sludge systems is fairly well understood now as a result of the work of a number of investigators both here and abroad. Downing and his colleagues at the Water Pollution Research Laboratory in England have contributed most significantly to this understanding. The basic requirement for maintaining a nitrifying flora in an activated sludge system is that the overall rate of sludge growth (and hence of sludge wasting) be no greater than the rate of growth of the nitrifying organisms. In a conventional system this requires relatively long cell residence times in order that much of the sludge produced as a result of the activity of the heterotrophs in removing carbonaceous material will be aerobically digested. However, for one reason or another, many plants which provide long cell residence times appear to be rather erratic in nitrifying. Just why this is so remains puzzling.

Barth and his colleagues at the Robert A. Taft Sanitary Engineering Center have worked with a two-stage activated sludge system which appeared to offer a number of advantages over the conventional one-stage systems where reliable nitrification is called for. In this system, the first aeration stage is devoted to removal of most of the carbonaceous material and the second stage largely to nitrification. By maintaining these two separate specialized sludges it is possible to achieve such long residence times in the second stage that nitrification will proceed even at relatively low temperatures without providing as long aeration times as would be needed in a conventional system.

After some comparative cost studies this two-stage system was recommended to the Sanitary District and was approved by them. To achieve the very low suspended solids and BOD concentrations called for, filters were provided following the second-stage clarifiers. Chlorination will be provided either before or after the filters to meet the coliform standard of the Illinois Sanitary Water Board.

Nutrient Removal

At present, the prescribed water quality standards do not require removal of either nitrogen or phosphorus, but this type of plant has the capability of providing for nutrient removal without appreciable additional capital cost. Such provisions have been made in the design of the plant.

Phosphate removal can be accomplished by adding an iron or aluminum salt to the first aeration stage. This has been studied by Barth and his colleagues as well as by a number of other investigators. At the Salt Creek plant provision has been made for such chemical additions.

Nitrogen removal by denitrification can be accomplished in the filters which follow the second-stage clarifiers by providing a carbon source to permit the development of a denitrifying flora in the filters. This process has been investigated at Pomona, California by the Federal Water Quality Administration and the Los Angeles County Sanitation District. Provisions for feeding methanol as a carbon source are included in the Salt Creek design.

It is not known to what extent nutrient removal will be practiced at Salt Creek, but it was relatively inexpensive to provide such capability.

Pilot Plant Studies

The Sanitary District was anxious to proceed immediately to final design of the Salt Creek plant after approval of our report in early 1968. The deadline for completion of final plans and specifications was December, 1969. Provisions were made to convert a one million gallon per day sewage treatment plant which the District operates at Hazelcrest, Illinois in southern Cook County to the type of process contemplated for Salt Creek. This was done and the plant was operated during part of 1969. It was not possible to develop a nitrifying flora until the sewage temperature reached about 60° F, but thereafter the plant operated smoothly with almost complete nitrification even after cold weather had reduced sewage temperatures to the 40's.

The nutrient removal facilities of the plant were tested to only a limited extent. No problems were experienced with phosphate removal by feeding sodium aluminate. The denitrification step encountered difficulties which were related more to equipment provided in the pilot plant than to the process. These should not be a problem in the full scale plants.

Plant Design

The design calls for the plant to handle an average flow of 30 mgd during dry weather with 50 mgd on maximum dry weather days. During wet weather 50 mgd will be given complete treatment. Wet weather flows above 50 mgd will receive sedimentation and chlorination. After coarse racks, pumping, screening and grit removal the sewage will flow to the first aeration stage which will provide three hours detention at 50 mgd. Sedimentation will be in circular clarifiers with an overflow rate of 1,450 gallons per day per square foot based on maximum day flow plus 30 percent sludge return. The second-stage clarifiers and sedimentation tanks will be the same as the first stage. Filters will have three feet of anthracite and sand media and will be designed to operate at six gallons per minute per square foot.

Sludge will be thickened in air flotation thickeners, digested and pumped to a land reclamation site. The Salt Creek plant will provide digestion facilities for sludge from another plant to be built in this part of the Sanitary District.

Chemical feeding facilities will permit feeding alum to the first aeration stage and also to the influent to the filters. Polyelectrolytes can also be fed as filter aids to the filter influent and to assist in sludge thickening. Methanol can be added to the filter influent if denitrification is desired. Chlorine can be added at a number of points in the system to deal with odor problems or to disinfect.

The plant is designed as the first stage of construction to be expanded ultimately to three times its initial size.

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